

# Reductive Dehalogenation of Bromoform in Aqueous Solution

Eric A. Betterton,<sup>1</sup> Robert G. Arnold,<sup>2</sup> Ronald J. Kuhler,<sup>2</sup> and Gregory A. Santo<sup>2</sup>

<sup>1</sup>Department of Civil Engineering and Engineering Mechanics; <sup>2</sup>Department of Atmospheric Sciences, University of Arizona, Tucson, Arizona

The hybrid semiconductor-macrocycle catalyst TiO<sub>2</sub>-cobalt phthalocyanine promotes the solar photolysis of aqueous bromoform under anaerobic conditions. The major decomposition products are dibromoethane and HBr. Bromomethane and methane were produced only after prolonged photolysis (30 hr). Acetone, derived from added 2-propanol, was the only observed oxidation product. Preliminary experiments showed that electrolytic reduction of aqueous carbon tetrachloride at a vitamin B<sub>12</sub>-modified silver electrode produced the expected lower homologues but with surprisingly high yields of methane. — Environ Health Perspect 103(Suppl 5):89–91 (1995)

Key words: TiO<sub>2</sub>, cobalt phthalocyanine, B<sub>12</sub>, bromoform, dehalogenation, electrolysis

## Introduction

Cobalt(I) [Co(I)] macrocycles, including phthalocyanines (TSP) and corrinoids (B<sub>12</sub>), are known to be exceptionally powerful nucleophiles that undergo rapid SN2 reactions with many halogenated hydrocarbons yielding organometallic complexes containing stable Co(III)-carbon  $\sigma$ -bonds. The metal-carbon bond is light sensitive, photolyzing rapidly to an alkyl radical and Co(II).

In the case of the hybrid semiconductor catalyst, titanium dioxide/cobalt phthalocyanine (TiO<sub>2</sub>-CoTSP), reductant is provided by the conduction band electrons ( $e_{CB}^-$ ) of the TiO<sub>2</sub> (1). Under bandgap illumination ( $\lambda < \approx 400$  nm), charge separation occurs. Valence band electrons are promoted to the conduction band where they can be trapped and made to do useful work, while the holes left in the valence band ( $h_{VB}^+$ ) are powerful oxidants that can react with electron donors adsorbed on the surface. In order to effectively retard

recombination of the  $e_{CB}^-$ - $h_{VB}^+$  pair, it is necessary for the electron- and hole-sinks to be physically adsorbed or chemically attached to the surface of the semiconductor (2–4). Hong et al. (1) have shown that by covalently linking CoTSP to the surface of TiO<sub>2</sub> using a silanizing agent, it is possible to relay a conduction band electron from the semiconductor to the metal center and reduce it to Co(I)TSP simply by exposure to sunlight under anaerobic conditions. The potential therefore exists for engineering a photocatalytic system in which sunlight could be used to generate a conduction band electron (i.e., reducing equivalents) and to cleave an organometallic bond, with the net result that the absorption of two photons by a hybrid catalyst could promote the catalytic reductive dehalogenation of an organic halide.

## Experimental Procedures

Detailed experimental procedures have been published elsewhere. Briefly, CoTSP was synthesized by the method of Day et al. (5), and the CoTSP hybrid catalyst, TiO<sub>2</sub>-CoTSP, was synthesized according to the method of Hong et al. (1). Experiments were conducted on cloud-free days over a period of 1 year. For Tucson (latitude 32°13'0"), the calculated solar fluxes over the 300 to 500 nm region at solar noon are  $6.9 \times 10^{16}$  and  $5.2 \times 10^{16}$  photons  $cm^{-2} s^{-1}$  at summer and winter solstice, respectively. Solar photolysis experiments were conducted by exposing a series of freshly prepared identical samples containing bromoform (CHBr<sub>3</sub>) in glass vials to sunlight. It should be noted that

CHBr<sub>3</sub> is subject to direct solar photolysis since the C-Br bond strength is 314 kJ mol<sup>-1</sup> ( $\approx 380$  nm). Therefore, our catalyzed dehalogenation results may contain a small contribution due to direct photolysis. Volatile organic species were determined by gas chromatographic analysis of the head space. Bromide concentration was determined by ion chromatography. A chemically modified electrode was made by dissolving vitamin B<sub>12</sub> in electrically conducting epoxy resin and coating a 6.5 cm<sup>2</sup> silver foil electrode with the mixture. The electrode was incorporated into a two-compartment electrolysis cell based on the design of Criddle and McCarty (6).

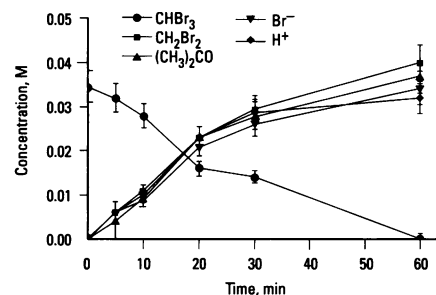
## TiO<sub>2</sub>-CoTSP System: Reaction Products and Stoichiometry

Head-space analysis of samples containing 1 mg/ml catalyst and 50% (v/v) 2-propanol that had been exposed to sunlight for up to 4 hr showed that CHBr<sub>3</sub> was degraded to its lower homologues, dibromomethane (CH<sub>2</sub>Br<sub>2</sub>) and bromomethane (CH<sub>3</sub>Br). Traces of methane were detected after photolysis for a total of approximately 30 hr. Acetone, derived from  $h_{VB}^+$  oxidation of 2-propanol, was also found, as were Br<sup>-</sup> and H<sup>+</sup>. The mass balance in Figure 1 indicates that all the major dehalogenation products were accounted for. The only significant halo-carbon species found during 1 hr of photolysis were CHBr<sub>3</sub> and CH<sub>2</sub>Br<sub>2</sub>. Although CH<sub>3</sub>Br and methane could be detected, their concentrations were insignificant compared to the higher homologues. Simultaneous head-space and

This paper was presented at the Conference on Biodegradation: Its Role in Reducing Toxicity and Exposure to Environmental Contaminants held 26–28 April 1993 in Research Triangle Park, North Carolina. Manuscript updated: fall 1994; manuscript received: January 23, 1995; manuscript accepted: February 13, 1995.

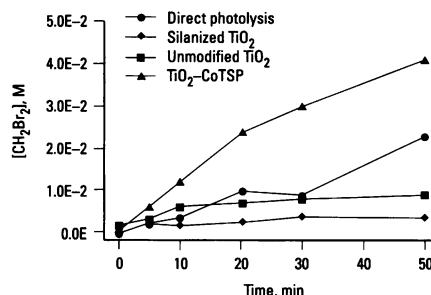
We thank the National Institute of Environmental Health Sciences for financial support and the Degussa Corporation for the gift of TiO<sub>2</sub>. We also thank Kara Warren for her able assistance in the laboratory.

Address correspondence to Dr. Eric A. Betterton, Department of Atmospheric Sciences, University of Arizona, Tucson, AZ 85721. Telephone (602) 621-2050. Fax (602) 621-6833.



**Figure 1.** Mass balance for reductive dehalogenation of bromoform in the presence of  $1 \text{ mg/l}^{-1}$   $\text{TiO}_2\text{-CoTSP}$  ( $[\text{CHBr}_3]_0 = 34 \text{ mM}$ ; 50% v/v aqueous 2-propanol; ambient temperature  $28^\circ\text{C}$ ; 4/23/92).

aqueous phase analysis (Figure 1) showed equimolar loss of  $\text{CHBr}_3$  and production of  $\text{CH}_2\text{Br}_2$ , acetone ( $(\text{CH}_3)_2\text{C=O}$ ),  $\text{Br}^-$  and  $\text{H}^+$ . Results of uncatalyzed photolysis experiments and experiments performed using silanized or unmodified  $\text{TiO}_2$  (Table 1) showed the same general features (loss of  $\text{CHBr}_3$ , production of  $\text{CH}_2\text{Br}_2$ ,  $(\text{CH}_3)_2\text{C=O}$ ,  $\text{Br}^-$  and  $\text{H}^+$ ) but at much lower rates (e.g., see the  $\text{CH}_2\text{Br}_2$  production rates in Figure 2). The approximate quantum yields using the hybrid catalyst, calculated as the initial rate of  $\text{CH}_2\text{Br}_2$  formation/photon flux into the vials, ranged

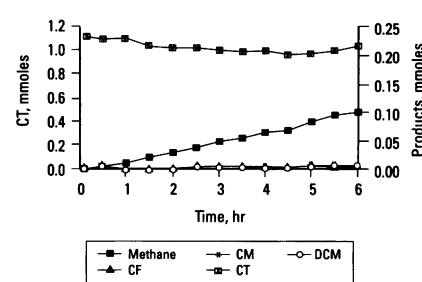


**Figure 2.** Rates of formation of  $\text{CH}_2\text{Br}_2$  for the four experimental systems tested in this work.

from 0.2 for  $1 \text{ mM}$   $[\text{CHBr}_3]_0$  to 1.0 for  $34 \text{ mM}$   $[\text{CHBr}_3]_0$ .

### $\text{B}_{12}$ -modified Silver Electrode: Preliminary Results

Figure 3 shows the results of an experiment during which  $1 \times 10^{-3}$  mole tetrachloromethane (CT) in 150 ml aqueous phosphate buffer was electrolyzed for 6 hr at an applied potential of 1.45 V using a  $\text{B}_{12}$ -coated silver electrode. Over this time, approximately 10% of the tetrachloromethane (CT) was reduced to methane ( $\text{CH}_4$ ) and approximately 1% appeared in the form of the lower homologues, trichloromethane chloroform (CF), dichloro-



**Figure 3.** Electrolysis of carbon tetrachloride in aqueous phosphate buffer at an applied potential of 1.45V.

methane (DCM), and chloromethane (CM). The mechanism of electroreduction has not yet been established.

### Conclusions

The hybrid  $\text{TiO}_2\text{-CoTSP}$  catalyst and the  $\text{B}_{12}$ -modified electrode are crude analogs for bacterially mediated reductive dehalogenation reactions. Although the synthetic and biochemical systems are heterogeneous in nature, the synthetic systems enjoy some potential engineering advantages:

- There is no need to supply a strong external reductant or remove residual reductant from a treated liquid phase. The catalyst can be conveniently separated from synthetic systems following treatment or it can be immobilized in a flow-through reactor.
- The overall thermodynamics of electron transfer for reductive dehalogenation can be conveniently manipulated over a considerable range by judicious selection of semiconductor, applied voltage, and macrocycle.
- Transport/uptake limitations inherent in whole-cell catalytic systems cannot impede the kinetics of reductive dehalogenation in the hybrid system, i.e., there are no physical barriers (membranes) between the target compound and the catalytic site.

**Table 1.** Initial rate of formation of  $\text{CH}_2\text{Br}_2$  for various experimental systems.

Catalyst, $1 \text{ mg ml}^{-1}$	Alcohol, 50% v/v	$[\text{CHBr}_3]_0$ , mM	Initial rate, <sup>a</sup> $\text{M min}^{-1} \times 10^4$
None (direct photolysis)	2-Propanol	34.0	$3.2 \pm 5$
		2.4	3.6
		1.7	2.4
		1.2	0.6
	1-Propanol	34.0	0.9
		34.0	1.0
Silanized $\text{TiO}_2$	Ethanol	34.0	0.2
	Methanol	34.0	0.5
	Ethylene glycol	34.0	0.5
	2-Propanol	34.0	$1.3 \pm 2$
		34.0	$2.8 \pm 7$
Unmodified $\text{TiO}_2$	1-Propanol	34.0	0.4
	Ethanol	34.0	$<1.2^b$
	Methanol	34.0	$<1.2^b$
	Ethylene glycol	34.0	0.9
	2-Propanol	34.0	$14.0 \pm 1$
$\text{TiO}_2\text{-CoTSP}$		17.0	14.0
		3.4	5.7
		2.4	7.1
		1.7	4.5
		1.2	3.0
		34.0	3.5
	1-Propanol	34.0	3.9
		34.0	1.0
	Ethanol	34.0	1.7
	Methanol	34.0	
	Ethylene glycol	34.0	

<sup>a</sup>The initial rate was calculated from the slope of the linear portion of the concentration–time plots for  $\text{CH}_2\text{Br}_2$  production over the first 10 to 20% of the reaction. The estimated uncertainty in each rate measurement is 20% unless otherwise indicated. <sup>b</sup>Formation of  $\text{CH}_2\text{Br}_2$  ceased after 5 min.

### REFERENCES

1. Hong AP, Bahnemann DW, Hoffmann MR. Cobalt(II) tetrasulphophthalocyanine on titanium dioxide: a new efficient electron relay for the photocatalytic formation and depletion of hydrogen peroxide in aqueous suspensions. *J Phys Chem* 91:2109–2117 (1987).
2. Henglein A. Colloidal  $\text{TiO}_2$  catalyzed photo- and radiation chemical

- processes in aqueous solution. *Ber Bunsen-ges Phys Chem* 86:241–246 (1982).
3. Kormann C, Bahnemann DW, Hoffmann MR. Photolysis of chloroform and other organic molecules in aqueous  $\text{TiO}_2$  suspensions. *J Environ Sci Technol* 25:494–500 (1991).
  4. Darwent JR, Lepre AJ. Interfacial electron transfer in colloidal  $\text{TiO}_2$  accelerated by surface adsorption and the electric double layer. *J Chem Soc Faraday Trans 2*:2323–2335 (1986).
  5. Day P, Hill HAO, Price MG. Some reactions of cobalt phthalocyanines. *J Chem Soc (A)*, 90–93 (1968).
  6. Criddle CS, McCarty PL. Electrolytic model system for reductive dehalogenation in aqueous environments. *Environ Sci Technol* 25:973–978 (1991).